

(12) UK Patent Application (19) GB (11) 2 185 936 (13) A

(43) Application published 5 Aug 1987

(21) Application No 8701934

(22) Date of filing 28 Jan 1987

(30) Priority data

(31) 8602493

(32) 1 Feb 1986

(33) GB

(71) Applicant
Silberline Ltd,

(Incorporated in United Kingdom),

Banbeath Industrial Estate, Leven, Fife KY8 5HD

(72) Inventor
Ian Robert Wheeler

(74) Agent and/or Address for Service
I. R. Wheeler, c/o Silberline Ltd, Banbeath Industrial Estate,
Leven, Fife KY8 5HD

(51) INT CL⁴
B32B 31/02 B29C 55/28 B32B 31/30

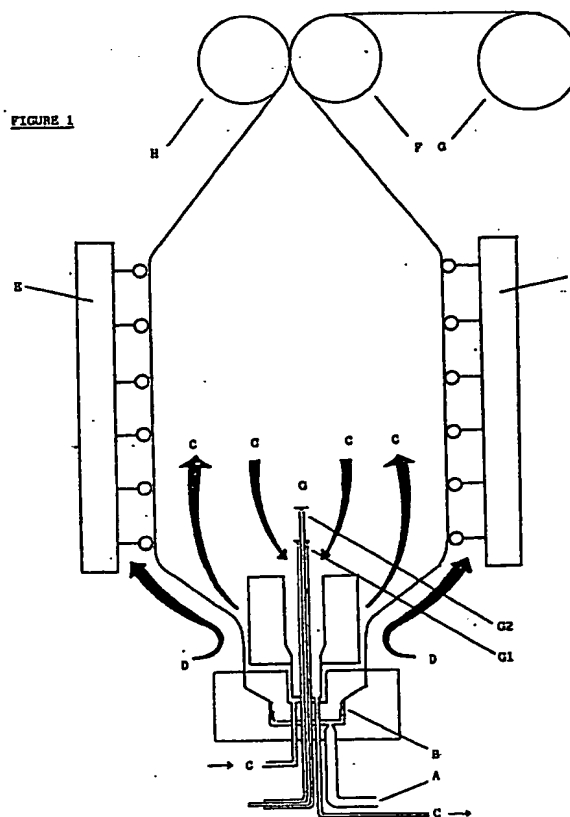
(52) Domestic classification (Edition I)
B5N 0172 2708 2730 2732 2734 2736 2740 3102 3130
B5B 351 352 35Y 360 363 367 368 FC
U1S 1814 3024 B5B B5N

(56) Documents cited
GB 1414785

(58) Field of search
B5N
Selected US specifications from IPC sub-class B32B

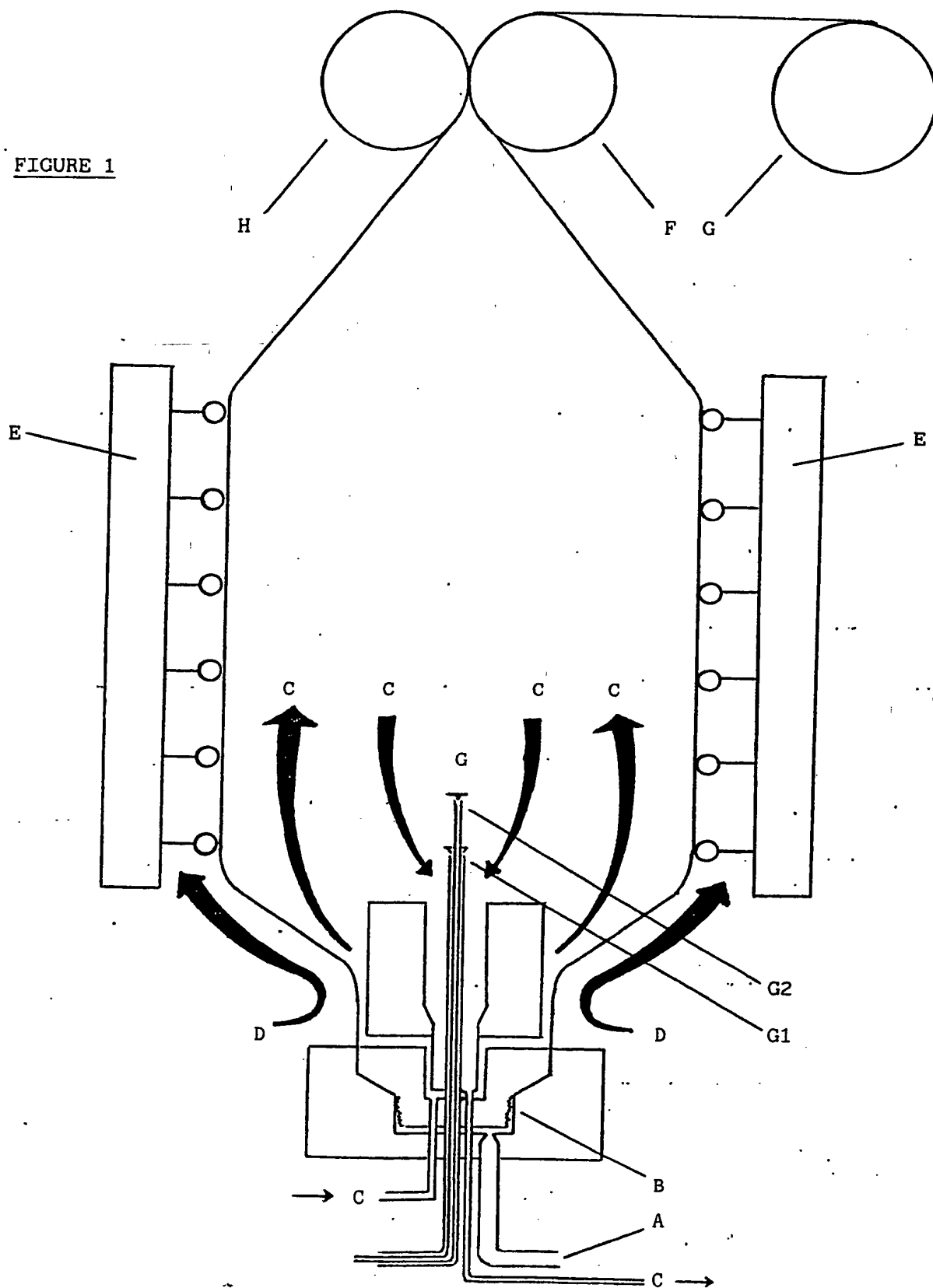
(54) Producing polymer film laminates

(57) A single stage, continuous process for the preparation of polymer film laminates having improved barrier properties to light and/or the migration of gases or liquids, comprising continuously applying by spray (G), one or more liquid coatings to the inside surface of the upwardly mobile polymer film bubble of a blown film machine and bonding together the coated surfaces at the spooling stage (F), (H), using a combination of pressure rollers and heat and/or electromagnetic radiation, thereby forming the laminate.



GB 2 185 936 A

FIGURE 1



SPECIFICATION

Method of producing polymer film laminates

- 5 This invention relates to polymer film laminates and a novel process for their preparation. More particularly, it concerns the manufacture of polymer film laminates simultaneously with blown film manufacture, within the polymer bubble of the blown film machine. 5
- Polymer film is used extensively in packaging applications, especially food packaging, where a barrier to moisture, air and/or light is essential to prevent deterioration of the food. Many common polymers, otherwise eminently suited to use in food packaging, by virtue for example, of transparency, high tear strength, solvent resistance and low cost, are nevertheless restricted in use by poor barrier properties. 10
- There are commercially available, polymers having very good barrier properties; for example, ethylene-vinyl alcohol copolymers containing at least 20% vinyl alcohol, which have a particularly low oxygen transmission rate, or polyvinylidenechloride (PVDC) which has a good resistance to water vapour transmission. Such polymers are however, expensive to produce and in some cases lack one or more of the other essential characteristics of packaging film. 15
- As a means of improving the barrier properties of such readily available, inexpensive polymers as polyethylene, polypropylene, ethylenevinyl acetate and PVC, it is well known to prepare polymer laminates. Polymers such as the immediately above mentioned, which, in other respects such as mechanical strength, are eminently suited for use as packaging films, have their barrier properties improved by bonding onto a second film having substantially improved barrier efficiency. This second film, which may be organic, such as another polymer, or inorganic, such as aluminium foil, is attached to the parent film by any suitable means. Heat, pressure and adhesives have all been used for this purpose. 20
- Amongst laminates of two or more dissimilar polymers, there may be mentioned the products of German patent 3008111 and Japanese patent 81/46731. 25
- One of the most barrier-efficient polymer laminates involves the bonding of thin aluminium foil using adhesives. Illustrating this process is the product of German patent 2324203. Whilst such a process excludes light, moisture and air from derived packaging, the foil, adhesives and lamination equipment required substantially increase the product cost. 30
- A similarly expensive process to achieve a metal film laminate is the so-called vacuum deposition process, in which a metal, often aluminium, is vaporised at reduced pressure and allowed to impregnate polymer film. Although the layer of deposited metal is very thin, typically sub-micron, the temperatures and vacuum required (1200-1300°C and 10⁻⁴ mm of mercury) are very expensive to achieve, particularly for a continuous process. Amongst recorded processes of this type, Japanese patents 79/95673 and 76/126278 are mentioned by way of illustration. 35
- Recognising the expense of existing film lamination processes, it is the object of the present invention to provide a process for the preparation of a highly efficient barrier film laminate in a single stage, low cost process. The process is effected simultaneously with preparation of the blown polymer film which itself comprises the outer surfaces of the laminate. 40
- The apparatus on which the process of the invention is performed is shown in Figure 1. In the conventional preparation of blown polymer film, the polymer, in powder or pellet form, is melted in the extruder (A) and continuously extruded through a circular die ring (B) to form an upwardly mobile polymer tube whose shape and rate of cooling are controlled by internal (C) and external (D) air currents and by external support elements (E). When the polymer has cooled sufficiently to be dimensionally stable, it is passed over a roller (F) and is thence spooled (G). The polymer film situated between the die (B) and the roller (F), which is termed the bubble, is kept constantly inflated by the balance between the internal air currents (C) and the external air current (D) and support elements (E). 45
- For operation of the process of the invention, the conventional blown film machine is modified by the addition of the following apparatus:-
- 50 a) One or more spray nozzles (G), each capable of delivering a liquid surface coating to the inner wall of the film bubble throughout 360° in a horizontal plane. The heights of the nozzles within the bubble should be adjustable. 50
- b) A second roller (H), forming a nip with roller (F). It is the function of the rollers (F) and (H) to bring the coated inner film surfaces together under pressure, thus forming the laminated product. Depending upon the selected mechanism of curing of the coating, it may be necessary to heat the pressure rollers or to install electromagnetic radiation generators in the area immediately adjacent to the rollers. 55
- Thus, as polymer is extruded and drawn up through the pressure rollers, one or more continuous coatings are sprayed onto the internal surface of the bubble. The coating is cured and bonded to the polymer film by pressure, heat and/or electromagnetic radiation. 60
- After forced cooling, if required, for example by forced air draught, the thus-formed laminate is collected on spool (G) in the conventional manner, with or without edge trimming, as desired. 60
- Amongst polymers suitable for blowing into film there may be mentioned polyolefins, such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), polypropylene (PP) and copolymers of these with minor amounts of such comonomers as ethyl acrylate and vinyl acetate. Also suitable are polyamide, 65
- polyvinyl chloride (PVC), polyvinylidene chloride, polyvinyl chloride-acetate copolymer, ethylene-vinyl

alcohol copolymer and polyesters, such as polyethylene terephthalate (PET).

Preferred polymers are those having active chemical groups capable of forming chemical bonds with one or more components of the sprayed liquid surface coating(s) during the coating curing stage. In this way, greater inter-layer strength of the laminate is achieved. Polymers having such active chemical groups may be used as the sole component of the blown film or may be co-extruded with inactive polymers such as polyethylene and polypropylene, where such blends are naturally compatible.

Coating systems suitable for the process of the invention contain at least one liquid component and, optionally, one or more solid components, soluble or insoluble in the liquid component(s). At least one of the components of the coating composition is capable of bonding physically, or more preferably, chemically to the polymer film surface. At least one of the components of the coating composition also has specific utility as a light, and/or migration barrier.

Though each liquid component of the system may be an inert solvent diluent, capable of being removed from the polymer bubble via the internal cooling aspirated air line (C), it is preferably itself capable of reaction with the polymer film surface, thereby contributing to the mechanical integrity and desirably, the barrier efficiency of the coating. Where chemically unreactive liquid diluents are required, for example to achieve a sprayable viscosity, such diluents are chosen for rapid release from the coating. Failure to achieve rapid release of the diluent results in residual bubbles in the laminated film. This may in turn lead to reduced barrier efficiency and/or mechanical strength. The release of diluents from the sprayed coating may be accelerated by the residual heat in the polymer film resulting from its extrusion.

Amongst reactive liquid diluents there may be mentioned mono and diisocyanates and liquid isocyanate prepolymers, hexamethoxymethylmelamine (HMMM) prepolymers, reactive polyamides, acrylates such as hexane diol diacrylate (HDDA), tetraethylene glycol diacrylate (TEGDA), tripropylene glycol diacrylate (TPGDA), trimethylol propane triacrylate (TMPTA) and trimethylol propane trimethacrylate (TMPTMA).

Unreactive liquid diluents are selected from compounds well known in the manufacture of liquid surface coatings, including aromatic and aliphatic hydrocarbons, alcohols, ketones, esters and water.

Solids capable of contributing to barrier properties and soluble or dispersible in one or more of the above mentioned liquid components of the coatings are, for example, urethanes and polyurethanes, including hydroxy terminated polyurethanes and urethane alkyds, polyester resins, isocyanate resins, including acrylic isocyanates, alkyd resins, rosin derivatives, nitrocellulose resins, cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP), polyamide, terpene and acrylic resins.

There may also be incorporated in the coating system, solid substances insoluble in any of the other components of the coating. Amongst these, there may be mentioned organic or inorganic pigments or mixtures thereof. Such pigments may confer an aesthetically pleasing appearance to the laminated film product in addition to any contribution to barrier properties.

Of particular note in this connection is aluminium flake pigment, which, in addition to its aesthetic properties, has considerable utility as a barrier to light and to the migration of liquids and gases through coatings in which it is incorporated. The so called leafing type of aluminium is preferred over the non-leafing variety in this application, due to the tendency of the former to form a network of roughly parallel, overlapping flakes at the surface of the coatings. When cured, this tends to form a more impenetrable barrier than that achieved from non-leafing flakes, which are more randomly distributed within the coating. Coatings containing the leafing type of flake are, however more difficult to bond together satisfactory than those containing non-leafing flake.

Where chemically inert polymers, such as the polyolefins, are used as the polymer film, the film surface may require activation for reaction with the sprayed liquid coating. Where the coating system presents no fire hazard, for example where it is water based, the inert polymer film may be corona discharged within the polymer film bubble to create chemically reactive surface sites.

Alternatively, the film surface may be activated by chemical means, for example using a peroxide. The peroxide may be conveniently applied by spray nozzle (G1) delivering liquid peroxide, optionally containing an inert solvent diluent, via a pipe passing vertically through the centre of the polymer extrusion die and concentric with a second pipe delivering the liquid coating via a second nozzle at a higher level (G2). As the polymer film rises from the die, it is coated first with peroxide and subsequently overcoated by the liquid coating.

The twin nozzle configuration may also be used to advantage to build a thick liquid coating film by applying two thin coatings of the same formulation. The release of inert solvent diluents is facilitated by the application of two thin coatings as opposed to one coating of the same combined thickness.

To ensure good adhesion of the film surface coating to itself when the blown film passes through the pressure rollers to form the laminate, the coating system(s) may contain a pressure sensitive or hot melt adhesive component, such as rosin derivatives, terpene and polyester resins.

Other agents well known in the art as adhesion promoters and crosslinking agents may be employed to improve the peel resistance of the laminated product. Amongst such compounds for inclusion in the coating system, there may be mentioned organic titanates, such as the Tilcom[®] range of TIL Ltd, or organic silanes such as those compounds available from Petrarch Systems Inc.

The rate at which each coating is sprayed and the rate of extrusion of the polymer film are chosen to achieve the desired degree of barrier efficiency at the minimum coating thickness, corresponding to the lowest cost. Such parameters may be determined by experiment for a chosen polymer and coating system.

The pressure applied by the laminating pressure rollers will also vary depending upon the nature of film and coating system and may again be determined by experiment. The optimum position for any spray head is generally at a height above that at which stretching of the blown film has substantially ceased.

The spray-applied coating(s) may be cured and bonded to the polymer film by heat or by electromagnetic radiation. As the polymer is generally heated to a temperature above 100°C and often above 150°C in the extruder in order to form the blown film, the surface coating is advantageously cured by the residual heat in the continuously blown film, thereby avoiding the expense of electromagnetic radiation curing equipment. Should the temperature of the film as it passes through the pressure rollers be too low to induce bonding of the coating surfaces, such bonding can again be achieved by the use of heated rollers or alternatively, by an electromagnetic radiation curing station in immediate proximity to the rollers. The laminated polymer film being continuously spooled thus has a high resistance to delamination.

It is the main advantage of the process of the invention that lamination is achieved simultaneously with film blowing in a continuous single stage process. The heat necessary for blown film formation can be utilised to cure the laminating layer. Any volatiles released from the coating system are contained within the film bubble and can be removed in a controlled manner via the exhaust air system, thereby avoiding pollution of the environment. Such volatiles may optionally be easily recovered for re-use.

It is a further advantage of the process of the invention that because two coated films are brought together, the chances of a film defect, such as a pinhole, extending through both coated films at the same position in the resulting laminate is statistically remote.

The products of the invention find particular use in all forms of packaging where impermeability to light, moisture and/or air is important. Nevertheless, depending upon the choice of polymer film and sprayed surface coating(s), the products may find wider use as barriers to electromagnetic radiation, liquids and/or gases.

The following example is further illustrative of the invention.

Example

Using the apparatus of Figure 1, a polymer blend comprising 95% low density polyethylene and 5% ethylene-vinyl alcohol copolymer (40 mol % ethylene) was blown at 190°C. A spray coating composition was prepared to the following formulation:-

30	Nitrocellulose DLX 3/5 undamped (I.C.I. PLC)	5.0	
	Unithane 672S/70 (Cray Valley Products Ltd)	7.2	
	Sparkle Silver 210-20-J 80% aluminium flake pigment in aldehyde resin (Silberline Ltd)	17.5	
35	Dicyclohexyl phthalate	5.5	
	Tilcom PI 2 titanate (TIL LTD)	0.8	
	Isopropanol	2.2	
	Industrial methylated spirits	20.6	
	Ethyl acetate	26.2	
40	Toluene	15.0	
		100.0	

Immediately after preparation, the coating system was delivered via the spray nozzle (G2) of Figure 1, to obtain a continuous coating of approx 40 µ thickness on the inner surface of the blown film, at a height at which the film was dimensionally stable.

The volatile solvents present in the formulation were continuously removed via the internal cooling aspirated air line (C). Curing of the film coating was effected partly by the residual heat of the blown film and partly by the pressure rollers.

The laminated film recovered on the product spool had a bright metallic appearance and good barrier properties to light, moisture and oxygen.

CLAIMS

1. A process for preparing a polymer film laminate, comprising, in a continuous process, the steps of:
 - a) applying by spray, one or more liquid coatings, to cover the entire inside surface of a polymer film bubble created by a blown film machine, said liquid coatings each comprising at least one liquid component and, optionally, one or more solid components, at least one of the liquid or solid components being (i) capable of physically, or preferably, chemically, bonding to both the polymer film surface and to itself and (ii), capable of promoting an improvement in the light and/or migration barrier properties of the polymer film.
 - b) Subjecting the upwardly mobile, coated polymer film, at a point where it is dimensionally stable and free of any non film-forming coating components, to pressure rollers, optionally assisted by heat or electromagnetic radiation, to effect a bond between the coated polymer surfaces, thereby forming a polymer film laminate having improved light and/or migration barrier resistance, compared to the untreated polymer film.

2. A process according to claim 1 in which the polymer film is prepared from a polyolefin or a polyolefin copolymerised or blended with a minor proportion of ethyl acrylate, vinyl acetate, vinyl chloride or vinyl alcohol monomer or polymer.
3. A process according to claim 1 in which the polymer film is prepared from polyvinyl chloride or polyvinyl chloride copolymerised or blended with a minor proportion of vinylidene chloride or vinyl acetate monomer or polymer. 5
4. A process according to claim 1 in which at least one liquid coating optionally contains a proportion of a pressure sensitive adhesive resin.
5. A process according to claim 4 in which the pressure sensitive adhesive component is a rosin derivative, a terpene resin or a polyester resin. 10
6. A process according to claim 1 in which at least one liquid optionally contains a resin selected from the group consisting of urethanes, polyesters, alkyds, rosin derivatives, isocyanates, nitrocellulose, cellulose, terpenes, acrylics and polyamides.
7. A process according to claim 1 in which at least one liquid coating optionally contains a solid or liquid radiation curable component. 15
8. A process according to claim 7 in which the solid or liquid radiation curable component is an acrylate monomer or prepolymer.
9. A process according to claim 1 in which at least one liquid coating optionally contains an organic or inorganic peroxide, an organic titanium derivative or an organic silicon derivative.
10. A process according to claim 1 in which the inside polymer film surface is optionally treated by corona discharge prior to spray coating. 20
11. A process according to claim 1 in which at least one liquid coating optionally contains a minor proportion of a metallic flake pigment.
12. A process according to claim 11 in which the metallic flake pigment is aluminium flake pigment.
13. A process according to claim 1 in which at least one liquid coating optionally contains an inert solvent, capable of being volatilised by the residual heat derived from extrusion of the polymer film. 25
14. A process according to claim 1 in which at least one liquid coating optionally contains a reactive liquid monomer, capable of being cured by electromagnetic radiation in the area immediately adjacent to the pressure rollers.
15. A polymer film laminate whenever prepared by any of claims 1-14. 30